

Hole Doping Effects on Spin-gapped $\text{Na}_2\text{Cu}_2\text{TeO}_6$ via Topochemical Na Deficiency

Kumiko MORIMOTO¹, Yutaka ITOH^{1*}, Kazuyoshi YOSHIMURA¹, Masaki KATO² and Ken HIROTA²

¹*Department of Chemistry, Graduate School of Science, Kyoto University, Kyoto 606-8502*

²*Department of Molecular Science and Technology, Faculty of Engineering, Doshisha University, Kyotanabe, Kyoto 610-0394, Japan*

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We report the magnetic susceptibility and NMR studies of a spin-gapped layered compound $\text{Na}_2\text{Cu}_2\text{TeO}_6$ (the spin gap $\Delta \sim 250$ K), the hole doping effect on the Cu_2TeO_6 plane via a topochemical Na deficiency by soft chemical treatment, and the static spin vacancy effect by nonmagnetic impurity Zn substitution for Cu. A finite Knight shift at the ^{125}Te site was observed for pure $\text{Na}_2\text{Cu}_2\text{TeO}_6$. The negative hyperfine coupling constant $^{125}A_{\text{tr}}$ is an evidence for the existence of a superexchange pathway of the Cu-O-Te-O-Cu bond. It turned out that both the Na deficiency and Zn impurities induce a Curie-type magnetism in the uniform spin susceptibility in an external magnetic field of 1 T, but only the Zn impurities enhance the low-temperature ^{23}Na nuclear spin-lattice relaxation rate whereas the Na deficiency suppresses it. A spin glass behavior was observed for the Na-deficient samples but not for the Zn-substituted samples. The dynamics of the unpaired moments of the doped holes are different from that of the spin vacancy in the spin-gapped Cu_2TeO_6 planes.

KEYWORDS: spin gap, $\text{Na}_2\text{Cu}_2\text{TeO}_6$, soft chemistry, hole doping, NMR

$\text{Na}_2\text{Cu}_2\text{TeO}_6$ is a spin-gapped layered compound and a Mott insulator.¹ Non-orthogonal spin dimers lie on Cu_2TeO_6 layers piled up with Na layers alternately. The uniform magnetic susceptibility χ shows a broad maximum at about $T_{\text{max}} = 160$ K and a spin gap $\Delta \sim 250$ K (Δ was estimated from Ref. [1]). Although the crystal structure is two-dimensional, the temperature dependence of χ indicates an alternating exchange Heisenberg chain. The large spin gap of about 250 K indicates the existence of a strong superexchange interaction on the Cu_2TeO_6 layers. Figure 1 illustrates the Cu_2TeO_6 plane of $\text{Na}_2\text{Cu}_2\text{TeO}_6$ and the J_1 - J_2 - J_3 superexchange pathways on the plane. According to Ref. [1], the alternating exchange interactions are predominant J_1 and the weaker $J_2 = 0.3J_1$. We address the following questions: whether the relatively long Cu-O-Te-O-Cu path actually bears such a strong superexchange interaction, and what kind of magnetic instability is behind the magnetic excitation spectrum with the large spin gap. The dynamics of the doped holes on the gapped magnetic excitation spectrum has attracted much attention as well as the hole-doped Néel ordering state.^{2,3}

In this paper, we studied the low-lying excitations of pure $\text{Na}_2\text{Cu}_2\text{TeO}_6$, the hole doping effect via a Na deficiency, and the spin vacancy effect via the Zn substitution of the Cu sites by means of magnetic susceptibility and NMR measurements. We obtained evidence of the existence of small covalency at the Te site by the ^{125}Te NMR technique. We succeeded in synthesizing the topotactic Na-deficient samples by soft chemical treatment, i.e., by a redox reaction with an oxidizer and the mother compound $\text{Na}_2\text{Cu}_2\text{TeO}_6$. The Na deficiency and the Zn substitution were found to induce Curie-type terms in their magnetic susceptibilities at low temperatures. No impurity-induced magnetic long range ordering

was confirmed for both the cases down to 2 K. For the Na-deficient samples, however, a spin-glass behavior was observed in the spin-gapped state at low temperatures, at the maximum of $T_g \sim 15$ K. The doped holes via the Na deficiency were found to induce competition among the interactions on the Cu_2TeO_6 layers.

Pure $\text{Na}_2\text{Cu}_2\text{TeO}_6$ samples were synthesized by a conventional solid state reaction method. The starting materials $-\text{Na}_2\text{CO}_3$, CuO , and TeO_2- were ground in a molar ratio of 1:2:1, pelletized, and heated at 680°C for 36 h in flowing oxygen gas. The resultant products were ground, repelletized, and heated under the same conditions. Zn-substituted samples were also synthesized by the solid state reaction method with ZnO as a starting material.

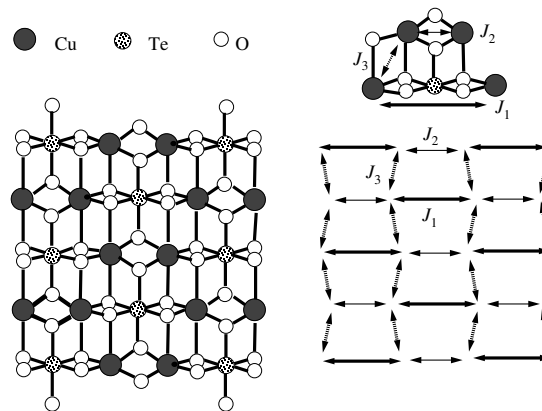


Fig. 1. Top view of a Cu_2TeO_6 plane of $\text{Na}_2\text{Cu}_2\text{TeO}_6$ (left panel). A schematic J_1 - J_2 - J_3 model illustrates the superexchange pathways according to Ref. [1].

*E-mail address: itoh@kuchem.kyoto-u.ac.jp

the soft chemical oxidation of the mother compound $\text{Na}_2\text{Cu}_2\text{TeO}_6$, using various concentrations of bromine as the oxidizing agent, similar to Na_xCoO_2 .⁴ $\text{Na}_2\text{Cu}_2\text{TeO}_6$ powder, typically 0.4 g, was stirred in 5 ml of a bromine solution in acetonitrile at 25 °C for 18 h. The products were washed several times with water and then with acetone to remove bromine and dried briefly under an ambient condition.

As the bromine concentration y increases as 1.0, 1.5, 1.6, 2.0, 2.5, 5.0, and 10 mol/L of Br_2/MeCN , the amount of Na deficiency increases, which was confirmed by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The typical value of the ratio of Na to Cu was estimated to be $(2 - \delta)/2 = 0.93$ (1.5 M) and 0.80 (2.5 M) within our technical accuracy of the ICP-AES. Because of the charge neutrality, the Na deficiency δ is compensated by the holes in the Cu_2TeO_6 plane; the nominal valence of Cu is then changed from 2 in the stoichiometric compound into $2 + \delta/2$. Thus, the nominal effective number p of unpaired moments per Cu was estimated to be $p = 0.07$ (1.5 M) and 0.20 (2.5 M).

Magnetic susceptibility was measured by a superconducting quantum interference device (SQUID) magnetometer. ^{65}Cu (nuclear spin $I = 3/2$), ^{23}Na ($I = 3/2$) and ^{125}Te ($I = 1/2$) NMR were performed by a pulsed NMR technique.

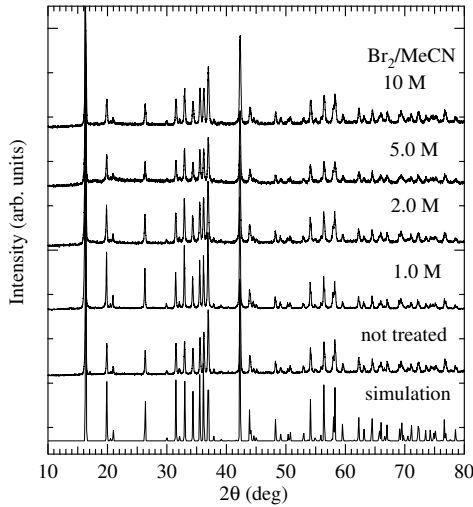


Fig. 2. Powder XRD patterns of the samples treated with Br_2/MeCN .

Figure 2 shows the powder X-ray diffraction (XRD) patterns of pure and Na-deficient samples. The powder XRD patterns show that the samples are in a single phase. As the bromine concentration increases, the individual lines of the XRD pattern are broadened and tend to shift to the lower angle side within the broad linewidth, indicating the effect of the nonstoichiometry of the Na deficiency.

Figure 3 shows the bulk magnetic susceptibility χ of pure $\text{Na}_2\text{Cu}_2\text{TeO}_6$. The magnetic susceptibility χ per for-

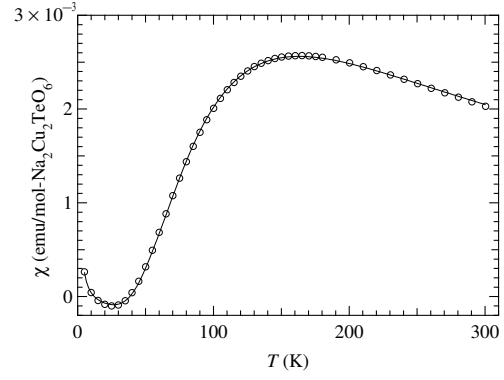


Fig. 3. Magnetic susceptibility of pure $\text{Na}_2\text{Cu}_2\text{TeO}_6$ at $H_0 = 1$ T. The solid curve is the least squares fit result by eq. (1).

mula unit is expressed by

$$\chi = 2\chi_s + \chi_0 + 2C/T, \quad (1)$$

where χ_s is the spin susceptibility, χ_0 is the temperature-independent magnetic susceptibility and should be the sum of the Van Vleck orbital susceptibility $2\chi_{\text{orb}}$ and the core-electron diamagnetic susceptibility $\chi_{\text{dia}} (= -0.116 \times 10^{-3} \text{ emu/mol-f.u.})$, and C/T is a Curie term. The numerical factor 2 represents two Cu ions per formula unit. We assumed the theoretical eq. (56a) in Ref. [5] for the $S = 1/2$ antiferromagnetic alternating-exchange Heisenberg chain as the spin susceptibility. Thus, χ_s is a function of the g -factor g , J_1 , and an alternation parameter $\alpha (\equiv J_2/J_1)$. The solid curve in Fig. 3 is the least squares fit result by eq. (1), where g , J_1 , α , χ_0 , and C are the fit parameters. We obtained $g = 2.23$, $J_1 = 262 \text{ K}$, $\alpha = 0.230$, $\chi_0 = -0.179 \times 10^{-3} \text{ emu/mol-f.u.}$, and $C = 1.09 \times 10^{-3} \text{ emu-K/mol-f.u.}$, which are consistent with the result in Ref. [1]. After Ref. [5], we obtained $\Delta = 243 \text{ K}$ from J_1 and α . The estimated χ_0 smaller than the calculated χ_{dia} might be due to the remnants of unreacted materials beyond our ICP-AES analysis.

Figure 4(a) shows the frequency-swept ^{125}Te NMR spectra of pure $\text{Na}_2\text{Cu}_2\text{TeO}_6$ in an external magnetic field of $H_0 = 7.48473 \text{ T}$ below $T_{\text{max}} = 160 \text{ K}$. Figure 4(b) shows the ^{125}Te Knight shift ^{125}K plotted against the magnetic susceptibility χ with temperature as an implicit parameter. The linear relation in the K - χ plot indicates that the spin Knight shift at the Te site results from the local magnetic polarization by the Cu electron spins

$$^{125}K_s = ^{125}A_{\text{tr}}\chi_s, \quad (2)$$

where $^{125}A_{\text{tr}}$ is a hyperfine coupling constant.

From Fig. 4(b), we estimated the hyperfine coupling constant of $^{125}A_{\text{tr}} = -43.7 \text{ kOe}/\mu_B$. Since $^{125}A_{\text{tr}}$ is nearly isotropic, the dipole field from Cu moments is not predominant at the Te site. An exchange polarization transfer mechanism to an empty orbital of the metal ion can yield such a negative hyperfine coupling.⁶ Thus, the J_1 - J_2 alternating superexchange chains in Fig. 1 can be a canonical model of $\text{Na}_2\text{Cu}_2\text{TeO}_6$.

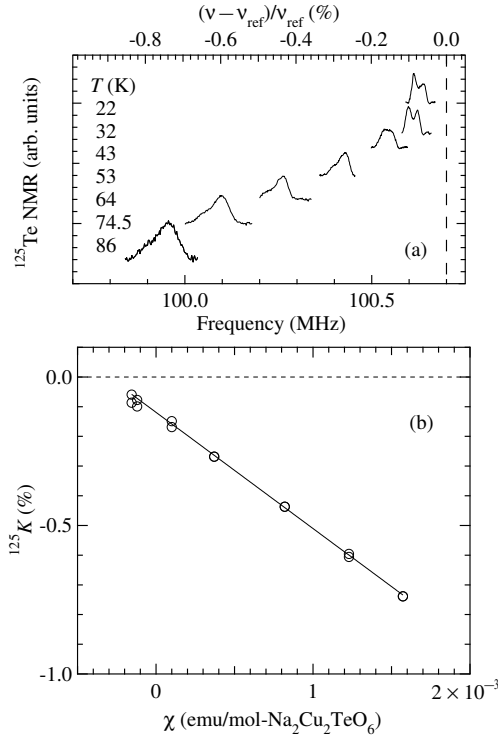


Fig. 4. (a) Frequency-swept ^{125}Te NMR spectra of pure $\text{Na}_2\text{Cu}_2\text{TeO}_6$ at $H_0 = 7.4847$ T below the peak temperature 160 K of the magnetic susceptibility χ . The dashed line is the reference resonance position $\nu_{\text{ref}} = 100.70$ MHz at H_0 . The nuclear gyromagnetic ratio $^{125}\gamma_n$ is assumed to be 13.454 MHz/T. The top axis represents the frequency shift defined by $(\nu - \nu_{\text{ref}})/\nu_{\text{ref}}$. A slight anisotropic powder pattern might result from the $5s^2$ lone pair of Te^{4+} ions. (b) ^{125}Te Knight shift ^{125}K plotted against magnetic susceptibility χ with temperature as an implicit parameter (K - χ plot).

Figures 5(a) and 5(b) show the effects of Na-deficiency and Zn-substitution on magnetic susceptibility χ for $\text{Na}_{2-\delta}\text{Cu}_2\text{TeO}_6$ treated with y mol/L of Br_2/MeCN ($y = 1.0, 1.6, 2.0$, and 5.0) and for $\text{Na}_2(\text{Cu}_{1-x}\text{Zn}_x)_2\text{TeO}_6$ with $x = 0.01, 0.02, 0.05$, and 0.15 at $H_0 = 1$ T, respectively. Both the Na deficiency and Zn impurities cause the Curie susceptibility at low temperatures. The Curie susceptibility induced by the Na deficiency in Fig. 5(a) is similar to the Na-deficient effect on $\text{Na}_x\text{V}_2\text{O}_5$.⁷

We fitted a Curie-Weiss law of $C/(T - \Theta)$ to reproduce the low-temperature χ in Fig. 5. For the Na-deficient samples, $|\Theta|$ increased as the bromine concentration increased, e.g., $\Theta \sim -2.3$ K for 1.6 M and -5.0 K for 2.0 M, whereas for the Zn-substituted samples, Θ was nearly zero. The results indicate that the doped holes are coupled with each other in the spin-gapped state, whereas the Zn-induced moments are nearly free. The Curie constants C for the Na-deficient samples were smaller than what would be expected from the effective hole number p in the ICP-AES analysis. For the Na-deficient and Zn-substituted samples with nearly the same Curie terms, the hole number p was larger than the Zn concentration x . The doped holes may not be well localized at specific sites on the Cu_2TeO_6 . For both the systems, the product of the maximum magnetic susceptibility χ_{max} and the

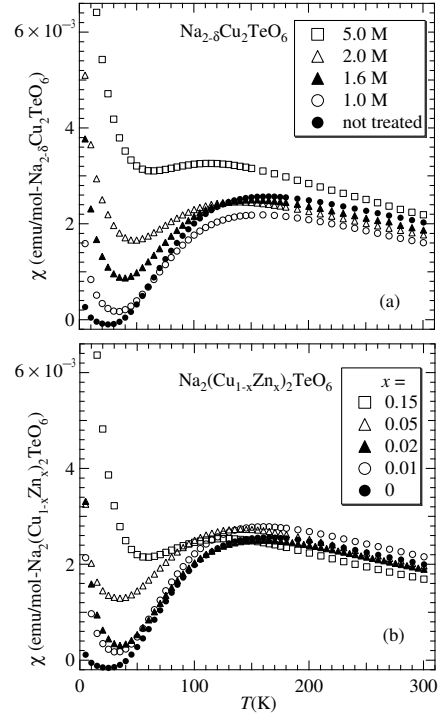


Fig. 5. (a) Magnetic susceptibility χ of $\text{Na}_{2-\delta}\text{Cu}_2\text{TeO}_6$ treated with y mol/L of Br_2/MeCN ($y = 1.0, 1.6, 2.0$, and 5.0) measured by the SQUID magnetometer at $H_0 = 1$ T. (b) Magnetic susceptibility χ of $\text{Na}_2(\text{Cu}_{1-x}\text{Zn}_x)_2\text{TeO}_6$ with $x = 0.01, 0.02, 0.05$, and 0.15 at 1 T. Both Na deficiency and Zn substitution cause a Curie magnetism at low temperatures.

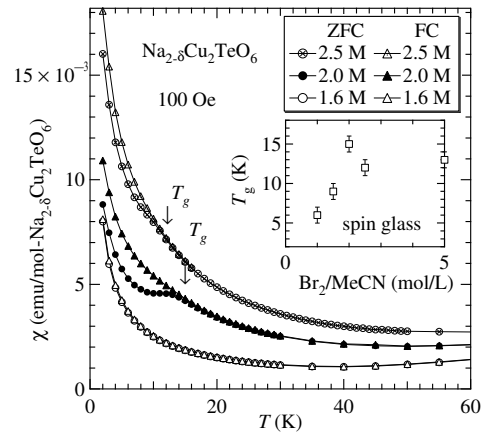


Fig. 6. Low-field hysteresis of magnetic susceptibility χ of $\text{Na}_{2-\delta}\text{Cu}_2\text{TeO}_6$ treated with y mol/L of Br_2/MeCN ($y = 1.6, 2.0$, and 2.5) after cooling in a zero magnetic field (ZFC) and an external magnetic field of 100 Oe (FC). Inset shows the spin glass temperature T_g against the bromine concentration y M.

maximum temperature T_{max} slowly decreased as the Na deficiency and Zn impurity increased.

Figure 6 shows the low-field hysteresis of the magnetic susceptibility χ of $\text{Na}_{2-\delta}\text{Cu}_2\text{TeO}_6$ treated with y mol/L of Br_2/MeCN ($y = 1.6, 2.0$, and 2.5), measured after cooling in a zero magnetic field (ZFC) and in a magnetic

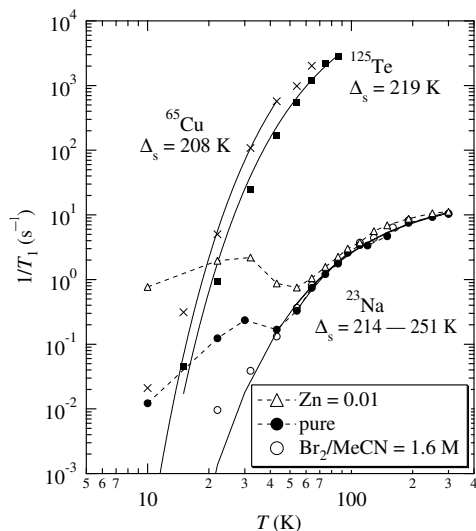


Fig. 7. Log-log plots of ^{23}Na nuclear spin-lattice relaxation rate $1/T_1$ against temperature for pure $\text{Na}_2\text{Cu}_2\text{TeO}_6$ (closed circles), Na-deficient $\text{Na}_{2-x}\text{Cu}_2\text{TeO}_6$ treated with 1.6 mol/L of Br_2/MeCN (open circles), and Zn-substituted $\text{Na}_2(\text{Cu}_{1-x}\text{Zn}_x)_2\text{TeO}_6$ with $x = 0.01$ (open triangles) at $H_0 = 7.4847$ T. For pure $\text{Na}_2\text{Cu}_2\text{TeO}_6$, ^{63}Cu (crosses) and ^{125}Te (closed squares) nuclear spin-lattice relaxation rates are also shown. The solid curves are the least squares fits by an activation function of $\exp(-\Delta_s/T)$. The estimated value of Δ_s slightly depends on the Cu, Te and Na sites and on the fit temperature ranges.

field of 100 Oe (FC). The magnetic hysteresis was easily suppressed by a high magnetic field. Thus, the bifurcation temperature may be regarded as a spin glass temperature T_g . For the sample with $y = 2.0$ M, $T_g = 14$ K up to $H_0 = 20$ Oe was suppressed by 1 T. The inset shows the spin glass temperature T_g against the bromine concentration y M. Such a spin glass behavior induced by doped holes is known for the hole-doped $\text{La}_{1.86}\text{Sr}_{0.04}\text{CuO}_4$ in a semiconducting regime.⁸ No hysteresis was observed for the Zn-substituted samples at 100 Oe.

In Fig. 7, the activation behaviors of the nuclear spin-lattice relaxation rates $1/T_1$ of ^{23}Na , ^{125}Te , and ^{63}Cu nuclear spins as a function of temperature were observed for $\text{Na}_2\text{Cu}_2\text{TeO}_6$, indicating the existence of a spin gap in the magnetic excitation spectrum. From the fits by a function of $\exp(-\Delta_s/T)$, we obtained the spin gap $\Delta_s = 208\text{--}251$ K, which is nearly the same as the gap $\Delta \sim 250$ K estimated from the static uniform spin susceptibility. The value of Δ_s slightly depends on the nuclear sites and on the fit temperature ranges.

In Fig. 7, a small peak behavior of $1/^{23}\text{T}_1$ in the spin-gapped state was observed for $\text{Na}_2\text{Cu}_2\text{TeO}_6$ at about 30 K, which has been frequently observed for quantum spin-gapped compounds, e.g., a Haldane gap compound.⁹ The peak behavior is explained by an additional nuclear spin-lattice relaxation induced by unpaired moments around defects or at crystal imperfections in the spin-gapped state. Using an electron spin-spin correlation function with a decay time τ_e , we have

$$1/T_1 = c^2 A^2 \frac{\tau_e}{1 + (2\pi\nu_{\text{res}}\tau_e)^2}, \quad (3)$$

where c is the number of “impurity” relaxation centers per unit volume, A is a nuclear-electron coupling constant, and ν_{res} is the NMR frequency.^{9–11} In the spin-gapped state, the lifetime τ_e of the impurity moment increases with cooling and then $\nu_{\text{res}}\tau_e = 1$ leads to a peak in $1/T_1$ of eq. (3). The absence of the peak behavior in $1/^{125}\text{T}_1$ and $1/^{63}\text{T}_1$ may be due to the large shifts of the impurity-neighbor Cu and Te NMR frequencies and the slow fluctuations of large hyperfine coupling constants A at the Te and Cu sites. The 30 K peak of $1/^{23}\text{T}_1$ is enhanced by Zn impurities, whereas it is suppressed by Na deficiency. One can consider that as the spin vacancy increases by Zn substitution, c increases but τ_e is invariant, whereas as the holes are doped by Na deficiency, c increases and τ_e largely changes. The static magnetic response to the spin vacancy is similar to that of the doped holes, while the dynamical response is different from each other. This difference may result from the hopping motion of the doped holes.

In conclusion, a finite covalency at the Te site in the Cu-O-Te-O-Cu bond was evidenced by the ^{125}Te Knight shift measurement of $\text{Na}_2\text{Cu}_2\text{TeO}_6$. We succeeded in introducing a topochemical Na deficiency by soft chemical treatment. It turned out that the spin dynamics of the doped holes through Na deficiency is different from that of the spin vacancy through Zn impurities.

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